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Preparation of calibration standard gas mixtures by primary gravimetric method: a case study on 960 μmol/mol of carbon dioxide in a nitrogen matrix

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Abstract

Calibration standard gas mixtures (CSGMs) are important reference standards that are necessary to achieve traceability for accurate and reliable gas measurement results. The CSGM of ~960 μmol/mol carbon dioxide (CO_2) in a nitrogen (N_2) matrix as the target concentration were prepared using a gravimetric method according to ISO 6142 with one dilution step. The CSGMs of ~2.8 % mol/mol CO_2 in N_2 were prepared and used as pre-mixtures. Verification of the CSGMs (pre-mixtures and target concentration) was conducted using a gas chromatographic thermal conductivity detector (GC-TCD). The results indicated that both the gravimetrical value and the analyzed value of CO_2 concentration where in good agreement. Excellent stability of the ~960 μmol/mol of CO_2 in N_2 CSGMs was shown during storage for a specified time. Such stability was characterized by a relative low uncertainty (0.177%) that was less than the required target uncertainty (0.250%). Additionally, determination of CO_2 concentration in a working standard (WS) gas mixture was done using two-point calibration and it generated higher precision than other methods. This implies that two-point calibration (bracketing technique) approach is a promising method that can be applied for quantification of the concentrations of sample gas mixtures in an international laboratory comparison held by the Asia Pacific Metrology Programme (APMP-QM-S15), and for certification of a WS.

Keywords: Carbon dioxide, Calibration standard gas mixture, Gravimetric method, Gas chromatographic, Traceability

1. Introduction

Gas analysis plays an important role in the field of chemical measurement in such areas as environmental monitoring, industrial safety, healthcare, and technological processes [1-3]. The accessibility of calibration standard gas mixtures (CSGMs) with traceable values to the international system of units (SI) and its uncertainty estimation are required to accomplish reliable and global comparability results in gas analysis [2, 4]. Consequently, preparation of the CSGMs to obtain high quality and traceable results in gas analysis is essential. [2, 5-7]. From the metrological point of view, the use of CSGMs is the basis for the traceability dissemination in the area of gas analysis. The CSGM establishes a gas measurement hierarchy that ensures measurement results are traceable in SI units through an unbroken chain, indicating that the CSGMs have taken a role as the standards of the quantity of gas composition [8-10].

Carbon dioxide (CO_2) is one of the important greenhouse gases. Its concentration has considerably increased in the atmosphere since the industrial revolution. The increases in global atmospheric CO_2 are mainly due to CO_2 emissions from the use of fossil fuels in transportation and electrical generation, gas flaring, and cement production. Other sources of CO_2 include the emissions due to land use changes

such as deforestation and burning biomass [11]. Currently, accurate and precise determination of the CO_2 concentration in the atmosphere has been given great attention by researchers. This is done to understand its potential impact on global climate change [12-13]. Therefore, accurate and precise monitoring of CO_2 emissions is required to obtain reliable information for evaluation of the global trend of increasing of CO_2 concentrations [13]. Various methods of measurement are available for monitoring the concentration atmospheric CO_2. These include Fourier Transform Infra-Red (FTIR) spectroscopy, Non-Dispersive Infra-Red (NDIR) gas analyzers [13], and gas chromatography (GC) [14], among others. Highly accurate and stable of CSGMs are needed for the calibration of the analytical instrumentations used for monitoring CO_2 at ambient and emission levels to assure reliable and traceable measurement of CO_2. The typical ambient (atmospheric level) and emissions (industrial stack and automotive) levels of CO_2 range from 380-400 μmol/mol [5] and 500-20,000 μmol/mol [15], respectively. In the international metrological network, quality assurance of gas analysis is implemented by participation in international laboratory comparison [2]. Laboratory comparisons of the quantification of CO_2 dealing with preparation of reference gas mixtures at atmospheric

and ambient levels were done [5]. The results of these comparisons not only show the measurement capabilities of participants at the level of the highest standard, but also establish the basis of confirmation of the suitability of the system of traceability assurance [2]. At the moment, the comparison of CO_2 in N_2 with a nominal amount of a substance at a level of 1000 µmol/mol has been proposed by regional bodies of the Asia Pacific Metrology Programme (APMP) with the code, APMP-QM-S15. The aim of the comparison is to support CO_2 in N_2 measurement capability for monitoring and controlling CO_2 emission from industry as well as automobiles [15]. Our institute, the RCM-LIPI as the national metrology institute of Indonesia, will take part in this international comparison to check our capability in measurement and calibration using our own CSGMs for the measurement of CO_2 in N_2 at emission levels including establish the traceability of gas analysis in Indonesia to SI units.

Numerous mixing methods have been reported for the preparation of CSGMs. They inlude gravimetric, volumetric, barometric, and dynamic methods [4, 7]. Among these methods, a gravimetric method is commonly used for the preparation of CSGMs. It has been used to produce CSGMs with high accuracy. Highly precise CSGMs can be achieved by gravimetrically weighing the smallest mass of a gas component and adding it to a mixture with minimal uncertainty [4]. Such gravimetric methods for the preparation of CSGMs are detailed in the ISO 6142 [10]. In a gravimetric method, in principle, the composition of gas mixtures is internationally traceable to mass standards and to pure parent gases. The composition of gas mixtures is expressed as a mole fraction that is determined based on the mass of gas filled into a high-pressure cylinder, the molar mass, and the purity of parent gases. The mass of each gas component filled into cylinder is calculated as the difference between the mass of the cylinder before and after filling it with a gas. The accuracy and precision of the gas mixture prepared relies on the weighing technique used, gas filling technique, and the quality of cylinders used [4]. The merit of a gravimetric method includes its small uncertainty, direct relation to SI through mass units, and the possibility to prepare the gas mixtures over a wide composition range.

In this paper, CSGMs of carbon dioxide (CO_2) in nitrogen (N_2) matrix at a concentration of ~960 µmol/mol were prepared using a gravimetric method to obtain highly accurate concentrations of CO2 with small uncertainty. This work was done to support the participation of our institute (RCM-LIPI) in international laboratory comparison in the field of measurement CO_2 in N_2 at emission level (1000 µmol/mol) held by APMP. The preparation target concentration of ~960 µmol/mol CO_2 in a N_2 matrix was obtained by dilution of 2.8% mol/mol of CO_2 in a N_2 matrix as pre-mixtures. Thus, a one-step dilution was used in this preparation scheme. The gravimetric concentration of CSGMs and their uncertainty were calculated according to ISO 6142. Verification of the concentration of prepared CSGMs was done by checking the internal consistency among the gas standard comparing the analyzed value by GC-TCD and the gravimetric value from this method of preparation. The concentrations of CSGMs were periodically monitored to investigate their stability in terms of gas concentration during storage. Additionally, another CSGM (working standard or WS) was prepared and its concentration was determined by fitting the analyzed value from GC-TCD

into the calibration curve produced using a series of CSGMs. Several calibrations approaches (multipoint, three-point, two-point and single point calibration) were compared to obtain a higher precision and accuracy of the CO_2 concentration in the CSGMs. Therefore, a higher degree of calibration accuracy can be proposed for certification of a WS.

2. Materials and methods

2.1 Materials

Two source gases, CO_2 and N_2, were used as the parent gases for each target gas concentrations. They were ultra-high purity grade. CO_2 gas (99.9995 % mol/mol of purity) was purchased from Air Liquide Company, Indonesia. The N_2 gas (99.9995% mol/mol of purity) was purchased from PT Surya Indotim Imex, Indonesia. The composition and concentration of the impurities contained in each parent gas were analyzed prior to use for the preparation of CSGMs.

2.2 Instruments

A GC (6890 series, Agilent Hewlett Packard, USA) equipped with a thermal conductivity detector (TCD) was used for the measurement of the CO_2 concentration in a N_2 matrix. The analytical measurement procedure and operating conditions of the GC-TCD were follows. The gas mixture was introduced into the GC system through a mass flow controller (MFC) Type 5890E (Brooks Instrument, USA) to maintain a constant gas flow rate. The MFC was installed before the injection line of the GC system. The flow rate of samples was set to 30 mL·min^{-1}. Samples of gas mixtures from the injection line was flowed through a 2 mL sample loop. The valve box temperature was maintained at 100 ºC. A stainless steel packed column (6 feet, 1/8" outer diameter, Porapak Q) was used for the separation of each component in the CSGMs. The column oven was set to a constant temperature of 40°C. Ultrahigh purity helium (He) (99.999% purity, Air Liquide Company, Indonesia) was used as carrier gas at a flow rate of 28 mL·min^{-1}. The detector temperature was kept at 250 °C. The flow rates of He as a reference and make up gas for the TCD were set to 20 and 7 mL·min^{-1}, respectively.

For the gravimetric preparation of the CSGMs, a mass comparator of type XP10003S (Mettler Toledo, Switzerland) was utilized. The mass comparator had 10 kg of maximum capacity and a 1 mg precision. It was placed on a granite slab and installed in an isolated chamber to minimize vibration and perturbation by air flow. Transfer of the component gas from CO_2 parent gas cylinder (pre-mixtures CO_2 in cylinder) and its dilution with pure N_2 were done using a gas filling station. The gas filling station was constructed with several components including diaphragm valves, ball valves, an electronic pressure gauge, stainless steel tubing (1/8" and 1/4" outer diameter), and a scroll pump. All connections to the gas filling station were of the VCR type to prevent leakage in the system. Moreover, the gases were filled into 2.5 L of high pressure aluminum cylinders at a 150 bar working pressure. Before filling the gases, the cylinder was evacuated and heated using a vacuum system (Model Hi-Cube 300 classic Pfeiffer, Germany) to clean the inside of the cylinder.

Table 1 Gravimetric concentration of CO_2 in CSGM and WS gas standards prepared in this study

Standard gas mixture	Cylinder ID	Concentration		Relative Uncertainty*
		CO_2	N_2	
Pre-mixtures	*(%mol/mol)*			
Pm-1	L150721009	2.779	Balance	0.302%
Pm-2	L150721002	2.799	Balance	0.302%
Pm-3	L150721004	2.811	Balance	0.298%
Pm-4	L150721010	2.822	Balance	0.295%
Target mixtures	*(μmol/mol)*			
CSGM-1	L150721005	949.276	Balance	0.590%
CSGM-2	L150721006	958.801	Balance	0.591%
CSGM-3	L150721016	975.231	Balance	0.591%
CSGM-4	L150721015	985.929	Balance	0.591%
WS	L150721012	965.597	Balance	0.593%

*Expanded relative uncertainty with a coverage factor of 2
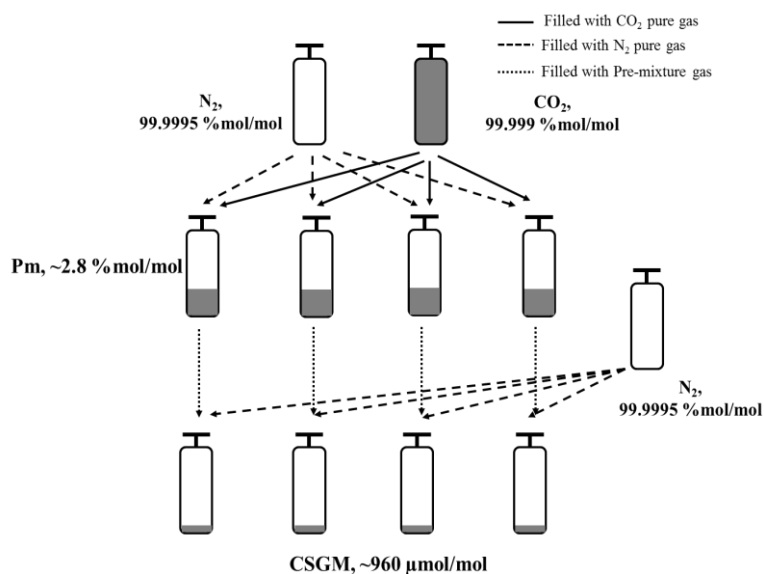
Figure 1 Preparation steps of four ~960 μmol/mol of CSGMs (CSGMs-1 through CSGM-4)

2.3 Preparation of calibration standard gas mixtures

The CSGMs were prepared using a gravimetric method in compliance with ISO 6142 [10]. This method is a primary method to assure international traceability for the preparation of CSGMs. Four CSGMs with nominal concentrations ~960 μmol/mol CO_2 in a N_2 matrix were individually prepared using gravimetric method based on the scheme shown in Figure 1. A single step dilution of CO_2 with N_2 was done. First, four ~2.8%mol/mol CO_2 gas samples in N_2 (Pm-1 through Pm-4) were prepared, at the exact concentrations shown in Table 1. These four CSGMs were then used to prepare another four CSGMs (CSGM-1 through CSGM-4) with a lower target concentration of ~960 μmol/mol (Table 1). The CSGMs were prepared using several steps. The quantities of CSGM and matrix gas required to obtain the target concentration were calculated based on the ISO 6142 standard.

The preparation step of WS gas mixtures was described previously [16]. The first step was a preparation of WS gas mixtures done by evacuating a 1 L aluminum cylinder to a pressure of less than 10^{-6} mbar. This condition was maintained for one day. During the evacuation, the cylinders were heated using a heating mantle at a temperature of 50 ℃ to remove any possible moisture on the inner surface of the cylinder. After that, a specified quantity (amount) of CSGM was filled into a 1 L aluminum cylinder and then diluted with highly pure N_2 gas. The gas filling station was used to transfer the gas from the CSGM and matrix gas into an aluminum cylinder. Subsequently, the amounts of CSGM and matrix gas filled into cylinder were accurately determined using a mass comparator at a controlled temperature (22±1 ℃) and humidity (50±5%). The weighing process was done by measuring the mass of the sample and tarred cylinder (reference cylinder containing 1 atm of N_2). The amounts of CSGM and matrix gas were determined from the difference between mass of sample and tarred cylinder. The purpose of using tarred cylinder in the gravimetric method was to correct for the buoyancy caused by ambient pressure that can affect the weighing process. After weighing, the cylinders containing the gas mixtures were homogenized by rotating the cylinder for one night using a cylinder homogenization system.

3. Results and discussion

3.1 Concentration and uncertainty calculations

The gravimetric concentrations of CSGMs in Table 1 were calculated on a molar basis [9-10] by applying the mathematical model expressed in Equation 1:

Table 2 Parameters of linearity established by the CSGMs

Parameters	Pre-mixtures (~2.8%mol/mol CO_2)	Target-mixtures (~960µmol/mol CO_2)
(n=7)		
LRE	y = 1004.1x +70.529	y = 0.127x + 7.323
R^2	0.9994	0.9994
p	4	4
RSD (%)	0.07;0.06;0.04;0.02	0.12; 0.13;0.15;0.09

n is number of measured replicates for each point in the calibration curve. LRE is linear regression equation expressed by formula y = mx+c (where x is the concentration of analyte in %mol/mol or µmol/mol, y is the peak area, m is the slope, and c is the intercept), p is number of points of each calibration curve, RSD is the relative standard deviation obtained for each point at calibration curve.

$$x_i = \frac{n_i}{n_i + n_{Balance}} \quad (1)$$

where x_i is the mole fraction of the gas component in the final CSGM, n_i is the mole of the target component gas, $n_{Balance}$ is the number of mole of the matrix or balance gas. Equation 2 was derived by applying the molecular weight of each gas component into Equation 1 [9-10] to realize the mole fraction:

$$x_i = \frac{\sum \langle \frac{m_i}{M_i}}{\frac{m_{Balance}}{M_{Balance}} + \sum_i \frac{m_i}{M_i}} \quad (2)$$

where m_i is the mass of the target gas component, M_i is the molecular weight of the target gas component, $m_{Balance}$ is the mass of balance gas added, and $M_{Balance}$ is the molecular weight of the balance gas.

The final uncertainty of the CSGMs, listed in Table 1, are associated with several parameters, including the gravimetric concentration, confirmation of the concentration by analysis and stability of the CSGMs. In this study, the gravimetric concentration of CSGMs was influenced by a number of uncertainty components including weighing of target component gas of CO_2, weighing of N_2 balance gas, the purity of CO_2, the purity of the N_2 as the balance (matrix) gas, molar masses of the gas components, and cylinder gas [4, 8]. A method for estimation of uncertainty in the gravimetric preparation gas been reported [16]. The uncertainties due to the confirmation of CSGMs concentration were determined from the variation of GC-TCD replicate analyses of the CSGMs and the uncertainty of the gravimetric concentration. A number of GC-TCD replicate analyses were conducted. At least seven replicates were done in all analytical runs. The uncertainty associated with analyzed concentration of CSGMs (μ_{anal}) can be calculated using Equation 3:

$$\mu_{anal} = \sqrt{(\mu_{grav})^2 + (s_{std1})^2 + (s_{std2})^2 + (s_{std3})^2 + (s_{std4})^2}$$

$$(3)$$

where μ_{grav} is the relative standard uncertainty of the gravimetric preparation of CSGMs, s is the relative standard uncertainty of n replicate measurements of CSGMs used in comparison (standard 1, 2, 3, and 4). The uncertainty due to the stability of CSGMs is specifically discussed below in the stability evaluation section.

3.2 Verification of the CSGMs

3.2.1 Identification of target component

Each component in CSGMs has to be clearly identified before the quantitative analysis is carried out. Optimization of the GC-TCD was done to obtain a good separation of CO_2 from the other components. The quantitative analysis of a component using a GC method is based on comparison of the peak area of a target component in sample and a standard. Consequently, co-elution of the target component (CO_2) with other components (such as N_2 as matrix) will cause inaccuracy in quantification of a target component in sample gas mixtures. The chromatogram in Figure 2 shows that CO_2 can be eluted at retention time 1.416 minutes with no interference from other components. The analytes in Figure 2 showed a high separation for determination of CO_2 with a resolution (R) value greater than 1.5 (R=1.805). High selectivity was also obtained with a good selectivity factor (α), 3.536.
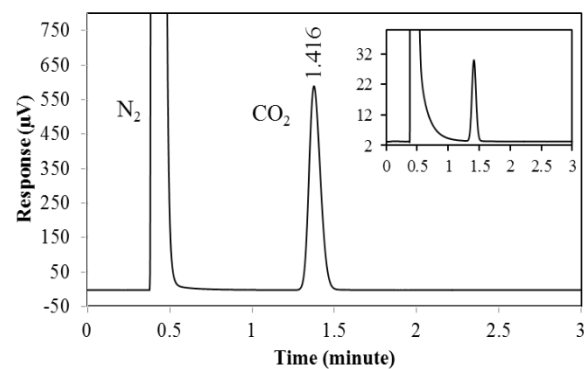
Figure 2 A GC-TCD chromatogram of a component gas in CSGMs made of ~2.8% CO_2 in N_2. The inset is a GC-TCD chromatogram is for ~960 µmol/mol CO_2 in N_2.

3.2.2 Internal consistency of the CSGMs concentration

The concentration of the prepared CSGMs (pre-mixture and target mixture), as listed in Table 1, verified the calculated concentration from gravimetric preparation and estimate the consistency of measurements on the gas mixture by an analytical method [8]. Since a traceable standards is not available for direct comparison with the prepared CSGMs, one indicator possibly might be used to verify the concentration of the target component in the mixture is demonstration of internal consistency among the prepared CSGMs [10, 17].

Table 3 Evaluation of stability of CSGMs between the CSGM-1 and L150721008

Interval of time (day)	CO_2 Concentration (µmol/mol)		Difference*	
	CSGM-1 (L150721005)	Stability acyl (L150721008)	(µmol/mol)	(%)
0	949.276	948.144	-1.132	-0.119
1	949.276	949.341	0.064	0.006
3	949.276	947.598	-1.679	-0.177

*Difference is (CO_2 concentration in CSGM-1) – (CO_2 concentration in L150721008)

In this study, the verification of CSGMs concentration was done using the GC-TCD. The peak area of the CO_2 component from the GC was plotted as a function of the mole fraction of the CSGMs. A response curve was constructed for the CO_2 gas component in the CSGMs (Table 2) to check the internal consistency among the prepared CSGMs. The response curve was developed using a least squares fit linear regression and coefficient of determination (R^2) was 0.9994 for both pre-mixtures and target mixtures, which is greater than 0.995. This indicates that the gravimetric values of those CSGMs (pre-mixtures and target mixtures) were consistently demonstrated. The detail of the procedures for the preparation CSGMs were appropriately carried out according to ISO 6142 [8].

The final value of repeatability must be 0.15% for verification of CSGMs. This value must be achieved to obtain the target relative uncertainty of CSGMs with less than the maximum value 0.25%. The target relative uncertainty of CSGMs is the final uncertainty of CSGMs originated from the uncertainty of weighing (gravimetric preparation), the verification result and stability testing of CSGMs. Table 2 presents the repeatability of measurements having concentrations within the range of 0.02-0.07% and 0.09-0.14% for pre-mixtures and target mixtures, respectively. These values meet the requirement of a final relative uncertainty of CSGMs that is less than 0.25%.

3.3. Stability of calibration standard gas mixtures

The concentration of prepared CSGMs must be repeatedly monitored within a specified period of time to confirm that neither chemical reaction nor adsorption/desorption of gas mixtures occurred inside the cylinders. Changes in the concentration of CSGMs may arise during their storage after certain time. There may be either significant chemical reactions or adsorption/desorption are occured. An equal division method was used to investigate the stability of the CSGMs. In this method, the gas mixture from one of the CSGMs (CSGM-1) was transferred into the empty cylinders (L150721008) until an equilibrium of pressure of the gas mixtures in both cylinders can be achieved. Subsequently, the concentration of gas components from both cylinders (CSGM-1 and L150721008) was determined using GC-TCD. Comparison of gas component concentrations in those two CSGMs was done over a specified time interval (0-3 days) to evaluate their stability. These results are shown in Table 3. From this table, the largest difference in the CO_2 concentrations of CSGM-1 and L150721008 samples was found to be 0.177% after three days. This value was used directly as a relative standard uncertainty for the estimation of uncertainty associated with the stability of CSGMs. The values were found to be less than the maximum limit for final uncertainty

of CSGMs i.e., 0.25%, indicating that the prepared CSGMs were stable.

3.4. Working standards measurement

Working standard (WS) gas mixtures (L150721012) were also gravimetrically prepared. The concentration CO_2 in the WS gas mixtures was quantitatively determined with a multipoint calibration curve using the prepared CSGMs. The results are presented in Figure 3.
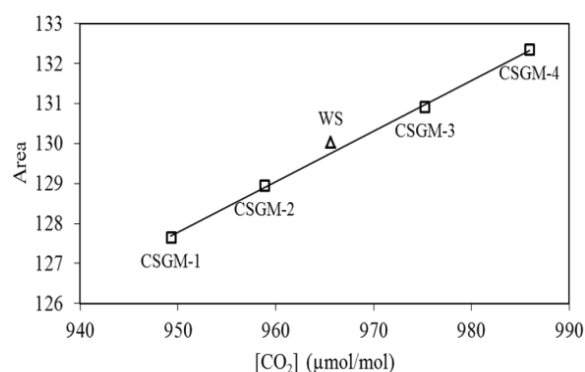
Figure 3 Peak area (from GC-TCD analysis) plot as a function of the mole fraction of a CSGM. The response of the WS gas mixture (L150721012) was plotted into a calibration curve of the CSGMs.

The calculated value of CO_2 concentration in WS gas mixtures were compared using various calibration methods including multi-point calibrations to identify the highest precision calibration method for determination of CO_2 concentration in WS gas mixtures. Three point, two point, and single point calibration results are summarized in Table 4. As can be seen from this table 4, a slight difference among calibration methods can be attributed to analytical error. A substantial difference in the calculated value was obtained when the single point method was used. There was a slight difference of about 0.004% when a two point calibration method (bracketing technique) was used, where two CSGMs (L006 and L016) had the closest concentrations relative to WS concentration were employed. This very low difference value implies that a two point calibration method (bracketing technique) was very effective. It has a high degree of accuracy in comparison to other methods for the determination of the CO_2 concentration in the WS. In addition to it ability to generate measurement data with good accuracy and reliability, the two-point calibration method was also successfully applied to determine the CO_2 concentrations in CSGMs considering faster measurement times.

Table 4 Comparison of various calibration methods for determining the CO_2 concentration in WS gas mixtures

Calibration methods	Calculated value µmol/mol	Difference*	
		µmol/mol	%
multipoint (4 point)	967.726		
Three point			
L005, L006, L016	968.107	0.381	0.039
L005, L016, L015	967.645	-0.081	-0.008
L006, L016, L015	967.470	-0.257	-0.027
Two point			
L006, L016	967.768	0.041	0.004
L005, L016	968.126	0.400	0.041
L006, L015	967.351	-0.375	-0.039
Single point			
L006	966.778	-0.949	-0.098
L016	968.579	0.853	0.088

*Difference from multipoint calibration method

From the verification of the CSGMs internal consistency, the stability study of the prepared CSGMs and their measurement uncertainty, it can be concluded that the prepared CO_2 in N_2 CSGMs of were suitable and feasible for use in analysis of sample of gas mixtures following the protocol of international laboratory comparison APMP-QM-S15. Additionally, the two point calibration method was selected for its highly accurate and precise determination of CO_2 concentrations in gas mixtures. Therefore, the proposed calibration method can be used in international laboratory comparison (APMP-QM-S15) to generate calibration curves for preliminary evaluation of CO_2 concentration in sample gas mixtures. Subsequently, the two CSGMs with concentrations of CO_2 close to that of the sample gas mixture were taken to do two-point calibration and determine the concentration of CO_2 with a higher degree of accuracy.

4. Conclusions

The results of this study indicate that CSGMs of ~960 µmol/mol CO_2 in N_2 matrix can be gravimetrically prepared and their CO_2 concentrations verified using GC-TCD. A single step dilution was used for gravimetric preparation. This was done to make such target mixtures (~960 µmol/mol of CO_2 in N_2). It was found that several gravimetrically prepared of CSGMs (pre-mixtures and target mixtures) showed very good agreement between the gravimetrically determined and analysed values. Comparison of CSGMs was done using least squares fit of the linear regression. The coefficients determination (R^2) of the linear regression curves for both pre-mixtures and target mixtures were found to be 0.9994. Stability evaluation of the CSGMs showed that the ~960 µmol/mol CO_2 samples were stable since the uncertainty of the stability of CSGMs (0.1768%) were less than the 0.25% target uncertainty. Moreover, the use of a two-point calibration method (bracketing tehnique) for the determination of CO_2 concentration in WS gas mixture is more suitable than the other methods because the bracketing technique can give higher precision. Accordingly, the bracketing technique is a recommended method calibration for determination of the concentrations of sample gases in mixtures in international laboratory comparisons (APMP-QM-S15) as well as for certification of a WS gas mixture.

5. Acknowledgement

6. References

[1] Budiman H, Zuas O. Validation of analytical method for determination high level carbon dioxide (CO_2) in nitrogen gas (N_2) matrix using gas chromatography thermal conductivity detector. Periodico Tchê Química. 2015;12(24):7-16.

[2] Rozhnov M, Levbarg O. A way of establishing quality of measurements in gas analysis—national and international aspects. Accred Qual Assur. 2007;12(8):415-7.

[3] Zuas O, Budiman H, Mulyana MR. Temperature effect on thermal conductivity detector in gases (carbon dioxide, propane and carbon monoxide) analysis : a gas chromatography experimental study. J Basic Appl Res Int. 2016;13(4):232-8.

[4] Milton MJT, Vargha GM, Brown AS. Gravimetric methods for the preparation of standard gas mixtures. Metrologia. 2011;48(5):R1–R9.

[5] Meane EAD, Plassa M, Rolle F, Sega M. Metrological traceability in gas analysis at I.N.R.I.M gravimetric primary gas mixtures. Accred Qual Assur. 2009;14:607-11.

[6] De Leer E. The metrological infrastructure for gas analysis. Accred Qual Assur. 2006;11:175-81.

[7] Geib RC. Calibration Standard Gases Are Key to Reliable Measurements. Specialty gas report. Montgomeryville: MathesonTri-Gas, Inc; 2005.

[8] Milton MJT, Guenther F, Miller WR, Brown AS. Validation of the gravimetric values and uncertainties of independently prepared primary standard gas mixtures. Metrologia. 2006;43:L7-L10.

[9] Wang L, Han Q. Primary reference materials and traceability chain for gas composition. Accred Qual Assur. 2002;7:217-9.

[10] International Organization for Standardization. ISO 6142:2001(E) Gas analysis-Preparation calibration gas

mixtures-Gravimetric method. 2nd ed. Geneva: ISO; 2001.

[11] Forster P, Ramaswamy V. Changes in atmospheric constituents and in radiative forcing. In: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M, Miller HL, editors. Contribution of working group I to the fourth assesment report of the interngovernmental panel of climate change. UK: Cambridge University Press; 2007. p. 129-234.

[12] World Meteorological Organization. TD No. 1077 Strategy for the implementation of the global atmosphere watch programme (2001-2007). Geneva: WMO-GAW; 2001.

[13] World Meteorological Organization. TD No. 1073 Global atmosphere watch meaurement guide. Geneva: WMO-GAW; 2001.

[14] Matsumoto N, Shimosaka T, Watanabe T, Kato K.

Evaluation of error sources in a gravimetric techique for preparation of a reference gas mixture (carbon dioxide in synthetic air). Anal Bioanal Chem. 2008;391(6):2061-9.

[15] Lee J. APMP-QM-S15 Protocol-Regional comparison carbon dioxide in nitrogen (1000 μmol/mol). Republik of Korea: Korea Research Institute for Standards and Sciences (KRISS); In press 2017.

[16] Budiman H, Mulyana MR, Zuas O. Gravimetric dilution of calibration gas mixtures (CO_2, CO, and CH_4 in He balance): toward their uncertainty estimation. AIP Conf Proc. 2017:1803:1-11.

[17] International Organization for Standardization. ISO 6143:2001(E) Gas analysis-Comparison methods for determining and checking the composition of calibration gas mixtures, 2nd ed. Geneva: ISO; 2001.